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COBALT(III) COMPLEXES

Numerous d^6 cobalt(III) complexes are known and have been studied extensively. Most of these complexes are octahedral in shape. Tetrahedral, planar and square antiprismatic complexes of cobalt(III) are also known, but there are very few. The most common ligands are ammonia, ethylenediamine and water. Halide ions, nitro (NO_2) groups, hydroxide (OH^-), cyanide (CN^-), and isothiocyanate (NCS^-) ions also form Co(III) complexes readily. Numerous complexes have been synthesized with several other ions and neutral molecular ligands, including carbonate, oxalate, trifluoroacetate and neutral ligands, such as pyridine, acetylacetone, ethylenediaminetetraacetic acid (EDTA), dimethylformamide, tetrahydrofuran, and trialkyl or arylphosphines. Also, several polynuclear bridging complexes of amido (NH_2^-), imido (NH^-), hydroxo (OH^-), and peroxy (O_2^{2-}) functional groups are known. Some typical Co(III) complexes are tabulated below:

Name	Formula
cobalt(III)hexammine chloride	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
chloropentamminecobalt(III) chloride	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
aquopentamminecobalt(III)	$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$
potassium hexacyanocobaltate(III)	$\text{K}_3[\text{Co}(\text{CN})_6]$
ammonium tetranitrodiammincobaltate(III)	$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
potassium hexanitrocobaltate(III)	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$
cyanocobalamine (Vitamin B-12)	$\text{C}_{63}\text{H}_{88}\text{CoN}_{14}\text{O}_{14}\text{P}$
barium hexacyanocobaltate(III) heptahydrate	$\text{Ba}_3[\text{Co}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$

The ammine complexes of Co^{3+} are prepared by adding excess ammonia to a solution of cobalt salt followed by air oxidation and boiling. The brown solution turns pink on boiling. The cyanide complexes are made by adding excess potassium cyanide to a solution of cobalt salt. Acidification of the solution with a small amount of acetic or hydrochloric acid followed by boiling yields $\text{K}_3\text{Co}(\text{CN})_6$. The aquo-halo mixed complexes are formed by stepwise substitution of H_2O molecule with halide ion in the coordination sphere. In general, a mixed complex may be prepared by substitution with a specific anion.

Alternatively, oxidation of a mixed solution of cobalt(II) halide-ammonium halide or cobalt(II) nitrate-ammonium nitrate in the presence of excess ammonia can form the amine complexes. Such oxidation may be carried out by passing air through the solution for several hours. The yield is high in the presence of activated charcoal.

COBALT(II) CYANIDE

[542-84-7]

Formula: $\text{Co}(\text{CN})_2$; MW 110.99; also forms a dihydrate, $\text{Co}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ [20427-11-6], MW 147.00 and a trihydrate $\text{Co}(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ [26292-31-9]

Synonym: cobaltous cyanide

Uses

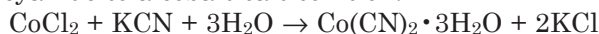
The compound has limited commercial applications. It is used as a catalyst and in the preparation of cyanide complexes.

Physical Properties

The anhydrous form is a deep-blue powder; hygroscopic; density 1.872 g/cm³; melts at 280°C; insoluble in water. The dihydrate is pink to reddish brown powder or needles; insoluble in water and acids; soluble in sodium or potassium cyanide solutions, ammonium hydroxide, and hydrochloric acid.

Preparation

The trihydrate salt is obtained as a reddish brown precipitate by adding potassium cyanide to a cobalt salt solution:



This on dehydration yields anhydrous Co(CN)₂. The Co(CN)₂·3H₂O precipitate formed above redissolves when excess KCN is added, forming a red solution of potassium cobalt(II) cyanide, K₄Co(CN)₆. Stoichiometric amount of KCN should, therefore, be used in the preparation of cobalt(II) cyanide.

Analysis

Elemental composition: Co 53.11%, C 21.64%, N 25.25%. Cobalt(II) cyanide is digested with nitric acid, brought into aqueous phase and analyzed for Co by various instrumental techniques. For estimating cyanide anion, a weighed amount of solid is treated with dilute sulfuric acid and distilled. The distillate (HCN) is collected over NaOH solution and the alkaline distillate is measured for cyanide by titration with a standard solution of AgNO₃ using dimethylaminobenzalrhodanine indicator. The distillate may be analyzed alternatively by colorimetry following treatment with chloramine-T and pyridine-barbituric acid; or by cyanide ion-selective electrode (APHA, AWWA and WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. Washington, DC: American Public Health Association).

Toxicity

The compound is highly toxic by ingestion and possibly through other routes of exposure.

COBALT(II) FLUORIDE

[10026-17-2]

Formula: CoF₂; MW 96.93; also forms di-, tri- and tetrahydrates.

Synonyms: cobaltous fluoride; cobalt difluoride

Uses

Cobalt(II) fluoride is used as a catalyst for organic reactions.

Physical Properties

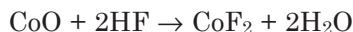
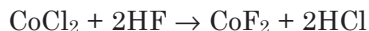
Red tetragonal crystal; density 4.46 g/cm³; melts at 1,127°C; vaporizes around 1,400°C; sparingly soluble in water; soluble in warm mineral acids; decomposes in boiling water. Tetrahydrate is red orthogonal crystal; density 2.22 g/cm³; decomposes on heating; soluble in water; di- and trihydrates are soluble in water.

Thermochemical Properties

ΔH_f°	-165.4 kcal/mol
ΔG_f°	-154.7 kcal/mol
S°	19.6 cal/degree mol
C_p	16.4 cal/degree mol
ΔH_{fus}	14.1 kcal/mol

Preparation

Cobalt(II) fluoride is prepared by heating anhydrous cobalt(II) chloride or oxide in a stream of hydrogen fluoride:



Also, cobalt(II) fluoride can be prepared as a tetrahydrate, $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ by dissolving cobalt(II) hydroxide in hydrofluoric acid. The tetrahydrate is then dehydrated to anhydrous fluoride. Elemental fluorine combines with cobalt at 450°C forming mixtures of cobalt(II)⁻ and cobalt(III) fluorides.

Analysis

Elemental composition: Co 60.80%, F 39.20%. Cobalt(II) fluoride is dissolved in hot nitric acid, the solution is appropriately diluted with water and analyzed for cobalt by AA or ICP spectrophotometry (see Cobalt). A small amount of salt dissolved in cold water (hot water may partially decompose forming oxyfluoride, $\text{CoF}_2 \cdot \text{CoO} \cdot \text{H}_2\text{O}$) may be analyzed for fluoride ion by fluoride ion-selective electrode or ion chromatography.

Toxicity

The compound is toxic by ingestion.

LD₅₀ oral (rat): 150 mg/kg

COBALT(III) FLUORIDE

[10026-18-3]

Formula: CoF_3 ; MW 115.93

Synonyms: cobaltic fluoride; cobalt trifluoride

Uses

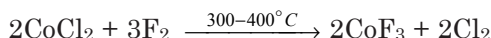
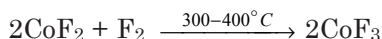
Cobalt(III) fluoride is used as a fluorinating agent for fluorination of hydrocarbons (Fowler process).

Physical Properties

Light brown hexagonal crystal; density 3.88 g/cm³; moisture sensitive; stable in dry air; melts at 927°C; reacts with water.

Preparation

Cobalt(III) fluoride may be prepared by reaction of elemental fluorine with cobalt(II) fluoride, cobalt(II) chloride or cobalt(III) oxide at 300 to 400°C.



It should be stored in a sealed glass ampule, free from moisture.

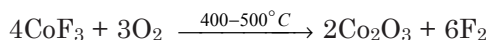
Electrolytic oxidation of cobalt(II) fluoride in 40% hydrofluoric acid yields hydrated cobalt(III) fluoride, $\text{CoF}_3 \cdot 3.5\text{H}_2\text{O}$ (3.5 is the stoichiometric amount of water per CoF_3 molecule in the crystal lattice).

Reactions

Cobalt(III) fluoride reacts with water forming a finely divided black precipitate of cobalt(III) hydroxide, $\text{Co}(\text{OH})_3$.

When heated with hydrogen at 400°C, it is reduced first to cobalt(II) fluoride and then to cobalt metal.

Heating with oxygen at 400 to 500°C converts the fluoride to oxide:



Anhydrous cobalt(III) fluoride reacts with many nonmetallic and metalloid elements including bromine, iodine, sulfur, phosphorus, carbon, arsenic, and silicon. It fluorinates these elements, and is reduced to Co^{2+} .

Analysis

Elemental composition: Co 50.83%, F 49.17%. Cobalt (III) fluoride may be digested with nitric acid and the resulting acid extract diluted with water and analyzed for cobalt by various instrumental techniques (see Cobalt). The compound may be identified from its reaction with water forming a black powder material.

Toxicity

Due to its high affinity for moisture, skin contact can cause irritation.

COBALT(II) HYDROXIDE

[21041-93-0]

Formula: $\text{Co}(\text{OH})_2$; MW 92.95

Synonyms: cobaltous hydroxide; cobaltous hydrate

Uses

Cobalt(II) hydroxide is used as a drier for paints and varnishes and is added to lithographic printing inks to enhance their drying properties. Other applications are in the preparation of cobalt salts; as a catalyst; and in storage battery electrodes.

Physical Properties

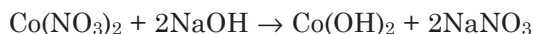
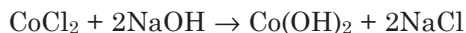
Two forms occur, a rose-red powder (more stable) and a bluish-green powder less stable than the red form; rhombohedral crystals; density 3.597 g/cm^3 ; decomposes on heating; practically insoluble in water 3.2 mg/L ; $K_{\text{sp}} 1.0 \times 10^{-15}$; soluble in acids and ammonia; insoluble in dilute alkalis.

Thermochemical Properties

ΔH_f°	-129.0 kcal/mol
ΔG_f°	-108.6 kcal/mol
S°	19.0 cal/degree mol

Preparation

Cobalt(II) hydroxide is obtained as a precipitate when an alkaline hydroxide is added to an aqueous solution of cobalt(II) salt:



Reactions

Thermal decomposition to cobaltous oxide, CoO , occurs at 168°C in a vacuum.

Cobalt(II) hydroxide is oxidized by air and other oxidizing agents, forming cobalt(III) hydroxide, $\text{Co}(\text{OH})_3$. Reactions with mineral acids produce corresponding Co^{2+} salts.

Analysis

Elemental composition: Co 63.40%, H 2.17%, O 34.43%. Cobalt(II) hydroxide is dissolved in nitric acid and the acid extract is analyzed for cobalt metal by AA, ICP or other instrumental techniques following appropriate dilution (see Cobalt).

COBALT(II) IODIDE

[15238-00-3]

Formula: CoI_2 ; MW 312.74; also forms a hexahydrate, $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$, MW 420.83

Synonyms: cobaltous iodide; cobalt diiodide

Uses

Cobalt(II) iodide is used for analysing water in organic solvents; and as a color indicator to determine moisture and humidity.

Physical Properties

Exists in two isomorphous forms, α - and β -forms; both modifications highly hygroscopic. The α -form is black hexagonal crystal; density 5.58 g/cm^3 ; turns dark green in air; melts at 560°C ; dissolves in water giving pink coloration. The α -forms sublimes in vacuo, partly forming an isomorous yellow modification—the anhydrous β -form.

The β -modification is a yellow powder; density 5.45 g/cm^3 ; converts to the α -form when heated to 400°C ; absorbs moisture from air, the yellow powder becoming green droplets; dissolves readily in water forming a colorless solution which turns pink on heating.

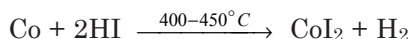
The hexahydrate is red hexagonal crystals; density 2.90 g/cm^3 ; loses water at 130°C giving anhydrous iodide; soluble in water, ethanol, acetone, chloroform and ether, forming colored solutions, (while the aqueous solution is red below 20°C and green above this temperature; the salt forms blue solution in ethanol, chloroform and ether).

Thermochemical Properties

$$\Delta H_f^\circ \quad -21.20 \text{ kcal/mol}$$

Preparation

Cobalt(II) iodide is prepared by heating cobalt powder in a stream of hydrogen iodide at 400 to 450°C :



The product obtained is the black crystalline α -form.

Cobalt(II) iodide also may be made by heating cobalt powder with iodine vapor.

Analysis

Elemental composition: Co 18.84%, I 81.16%. CoI_2 may be identified from its varying colors in different solvents. Under varying conditions, its aqueous solution may be analyzed for cobalt by AA, ICP or other instrumental techniques after appropriate dilution (see Cobalt). Iodide anion may be analyzed in sufficiently diluted aqueous phase by ion chromatography. Also, the analy-

sis of the compound dissolved in chloroform or acetone at low ppm concentration may be performed by GC/MS. The presence of characteristic iodide anion mass, 127 amu, in the mass spectra serves as a further confirmatory test.

COBALT(II) NITRATE

[10141-05-6]

Formula: $\text{Co}(\text{NO}_3)_2$; MW 182.94; occurs in common hexahydrate form, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [10026-26-9], MW 291.03

Uses

Cobalt nitrate is used in the decoration of porcelain and stones; in the manufacture of invisible inks and cobalt pigments; in hair dyes; in animal feeds; as an additive to soils; in catalysts preparation; and in vitamin supplements.

Physical Properties

The hexahydrate is red monoclinic crystal; deliquescent in moist air; density 1.87 g/cm³; decomposes at 55°C, losing three molecules of water; decomposes to green cobalt(II) oxide on further heating at 74°C; very soluble in water (134 g/100mL at 0°C); also soluble in alcohols and acetone.

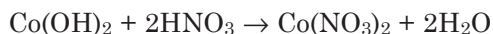
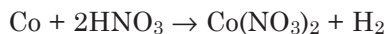
The anhydrous salt is pale red powder; density 2.49 g/cm³; decomposes around 100°C; soluble in water.

Thermochemical Properties

$$\Delta H_f^\circ \quad -100.50 \text{ kcal/mol}$$

Preparation

Cobalt(II) nitrate is prepared by treating the metal, or its oxide, hydroxide or carbonate with dilute nitric acid. The solution on evaporation yields red crystals of hexahydrate:



Analysis

Elemental composition (anhydrous salt): Co 32.33%, N 15.31%, O 52.47%. The aqueous solution may be analyzed for cobalt by AA or ICP or other instrumental methods. The nitrate anion may be measured by ion chromatography or nitrate ion-selective electrode. The solutions may require sufficient dilution for all these measurements.

Toxicity

The compound is toxic by oral, subcutaneous, and intravenous routes.

LDL₀ oral (rabbit): 250 mg/kg

LDL₀ subcutaneous (rabbit): 75 mg/kg

COBALT OCTACARBONYL

[10210-68-1]

Formula: Co₂(CO)₈; MW 341.95

Synonyms: dicobalt octacarbonyl; cobalt carbonyl; cobalt tetracarbonyl dimer

Uses

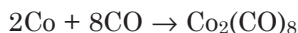
Cobalt octacarbonyl is used as a catalyst in the Oxo process (see Carbon Monoxide). It also is used as a catalyst for hydrogenation, isomerization, hydrosilation and polymerization reactions. The compound is also a source of producing pure cobalt metal and its purified salts.

Physical Properties

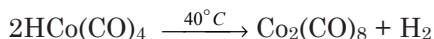
Orange crystals; density 1.78 g/cm³; melts at 51°C; decomposes above this temperature; insoluble in water; soluble in most organic solvents including alcohol, ether, carbon disulfide.

Preparation

Cobalt octacarbonyl is prepared by the reaction of finely divided cobalt with carbon monoxide under pressure:



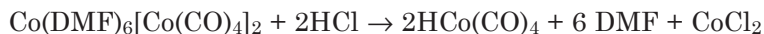
The compound may be prepared in a similar way from cobalt(II) iodide. Also, it may be prepared by thermal decomposition of cobalt carbonyl hydride:

**Reactions**

Cobalt octacarbonyl forms complexes with many types of ligands, replacing one or more CO groups.

Reaction with potassium cyanide forms a cyano derivative that probably has the structure K₃[Co(CN)₅(CO)].

Reaction with ammonia forms ammine salt, [Co(NH₃)₆][Co(CO)₄]₂ liberating carbon monoxide (Hieber, W. and H. Schulten. 1937. *Z. Anorg. Allgem. Chem.*, 236, p. 17). In a strongly alkaline solution, cobalt octacarbonyl undergoes hydrolysis, forming cobalt carbonyl hydride. This hydride, used in organic synthesis as a catalyst, may be prepared in a solution of hexane or toluene by adding octacarbonyl to dimethylformamide (DMF), followed by acidification:



Metal derivatives of cobalt carbonyl hydride such as $\text{Ti}[\text{Co}(\text{CO})_4]$, $\text{Zn}[\text{Co}(\text{CO})_4]_2$, or $\text{Cd}[\text{Co}(\text{CO})_4]_2$ are formed upon reaction of cobalt octacarbonyl with these metals in the presence of carbon monoxide under pressure. Reaction with halogens (X) produces cobalt carbonyl halides, $\text{Co}(\text{CO})\text{X}_2$.

Cobalt octacarbonyl decomposes when treated with nitric acid, forming cobalt nitrate. A similar reaction occurs with sulfuric acid or hydrochloric acid, but at a slower rate.

Analysis

Elemental composition: Co 32.47%, C 28.10%, O 37.43%. Cobalt octacarbonyl may be digested with nitric acid, diluted appropriately, and analyzed by AA, ICP, or other instrumental methods (see Cobalt). The compound may be dissolved in methanol and the solution analyzed by GC/MS.

Toxicity

Cobalt octacarbonyl is toxic by ingestion, inhalation, and other routes of exposure.

LD_{50} intraperitoneal (mice): 378 mg/kg

COBALT(II) OXIDE

[1307-96-6]

Formula: CoO ; MW 74.932

Synonyms: cobaltous oxide; cobalt monoxide

Uses

Cobalt(II) oxide is used as a pigment for ceramics and paints; for drying paints, varnishes and oils; for coloring glass; as a catalyst; and for preparation of other cobalt salts. The commercial product is a mixture of cobalt oxides.

Physical Properties

The commercial product is usually dark grey powder, but the color may vary from olive green to brown depending on particle size; density 6.44 g/cm^3 , which also may vary between 5.7 to 6.7 g/cm^3 , depending on the method of preparation; melts around $1,830^\circ\text{C}$; insoluble in water; soluble in acids and alkalis.

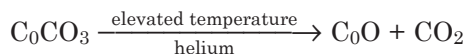
Thermochemical Properties

ΔH_f°	-56.86 kcal/mol
ΔG_f°	-51.19 kcal/mol

S°	12.67 cal/degree mol
C_p	13.19 cal/degree mol

Preparation

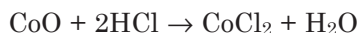
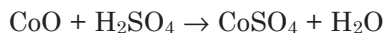
Cobalt(II) oxide is prepared by heating cobalt(II) carbonate, CoCO_3 , cobalt(III) oxide, Co_2O_3 or tricobalt tetroxide, Co_3O_4 , at high temperatures in a neutral or slightly reducing atmosphere:



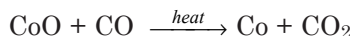
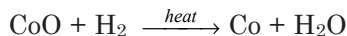
Reactions

Cobalt(II) oxide readily absorbs oxygen at ordinary temperatures. Heating at low temperatures with oxygen yields cobalt(III) oxide.

Cobalt(II) oxide reacts with acids forming their cobalt(II) salts. Reactions with sulfuric, hydrochloric and nitric acids yield sulfate, chloride and nitrate salts, respectively, obtained after the evaporation of the solution:



Reactions with alkali hydroxide yield cobalt(II) hydroxide. Cobalt(II) oxide is readily reduced by hydrogen, carbon or carbon monoxide to cobalt:



It combines with silica in molten states under electrothermal heating to produce silicate, $\text{CoO} \cdot \text{SiO}_2$.

Analysis

Elemental composition: Co 78.65%, O 21.35%. The commercial product generally contains 76% Co. The powder is digested with nitric acid and the acid extract, after dilution, is analyzed for Co by various instrumental techniques (see Cobalt). Cobalt(II) oxide may be analyzed by x-ray directly, without acid digestion.

Toxicity

Cobalt(II) oxide is moderately toxic by ingestion and subcutaneous and intratracheal routes.

LD₅₀ oral (rat): 202 mg/kg

COBALT(III) OXIDE

[1308-04-9]

Formula: Co_2O_3 ; MW 165.86

Synonyms: cobaltic oxide; cobalt trioxide; dicobalt trioxide; cobalt sesquioxide

Uses

Cobalt(III) oxide is used as a pigment; for glazing porcelain and pottery; and for coloring enamels.

Physical Properties

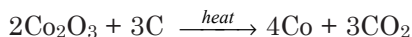
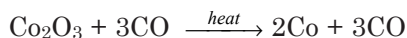
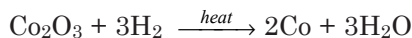
Grayish black powder; density 5.18 g/cm³; decomposes at 895°C; insoluble in water; soluble in concentrated mineral acids.

Preparation

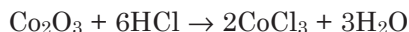
Cobalt(III) oxide is prepared by heating cobalt compounds at low temperatures in air.

Reactions

Heating with hydrogen, carbon or carbon monoxide reduces the oxide to cobalt metal.



Strong heating in air converts cobalt(III) oxide to tricobalt tetroxide. Reactions with mineral acids produce their Co^{3+} salts:

**Analysis**

Elemental Composition: Co 71.06%, O 28.94%. Cobalt may be analyzed in acidified solutions by various instrumental techniques (see Cobalt).

COBALT(II) SULFATE

[10124-43-3]

Formula: CoSO_4 ; MW 155.00; the commercial form is heptahydrate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ [10026-24-1]; also forms a monohydrate, $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ [13455-34-0]

Synonym: cobaltous sulfate

Uses

Cobalt(II) sulfate is used in storage batteries and electroplating baths for cobalt. It also is used as a dryer for lithographic inks; in pigments for decorating porcelains; in ceramics, glazes and enamels to protect from discoloring; and as a additive to soils.

Physical Properties

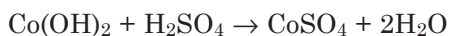
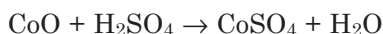
The anhydrous salt of cobalt(II) sulfate is a red orthogonal crystal; density 3.71 g/cm³; melts above 700°C; the monohydrate is red orthogonal crystal having a density of 3.08 g/cm³; the heptahydrate is a pink salt, monoclinic prismatic crystals, density 2.03 g/cm³; heptahydrate dehydrates to hexahydrate at 41°C and converts to monohydrate at 74°C; the anhydrous salt and heptahydrates are soluble in water; monohydrate slowly dissolves in boiling water.

Thermochemical Properties

ΔH_f°	-212.3 kcal/mol
ΔG_f°	-187.0 kcal/mol
S°	28.2 cal/degree mol

Preparation

Cobalt(II) sulfate is prepared by dissolving cobalt(II) oxide, hydroxide or carbonate in dilute sulfuric acid, followed by crystallization:



Crystallization yields the commercial product, pink heptahydrate. Further oxidation of this salt in dilute H₂SO₄ with ozone or fluorine produces hydrated cobalt(III) sulfate, Co₂(SO₄)₃·18H₂O. This blue octadecahydrate, Co₂(SO₄)₃·18H₂O also is obtained by electrolytic oxidation of cobalt(II) chloride or any cobalt(II) salt solution in 8M sulfuric acid.

Analysis

Elemental composition: Co 38.03%, S 20.68%, O 41.29%. Solid cobalt(II) sulfate is brought to aqueous phase by acid digestion, appropriately diluted, and analyzed for cobalt by flame or furnace AA or ICP. It also may be determined in the solid crystalline form by x-ray methods. The sulfate anion may be measured by dissolving an accurately measured small amount of salt in measured quantities of water and analyzing the solution by ion chromatography.

COBALT SULFIDES

Occurrence and Uses

Cobalt forms four sulfides: (1) cobalt(II) sulfide or cobaltous sulfide, CoS , MW 91.00, CAS [1317-42-6]. (2) cobalt(III) sulfide or cobaltic sulfide, or cobalt sesquisulfide, Co_2S_3 , MW 214.06, CAS [1332-71-4] (3) cobalt disulfide, CoS_2 , MW 123.05. (4) tricobalt tetrasulfide, Co_3S_4 , MW 305.04

Among these sulfides, only the ordinary cobalt(II) sulfide, CoS has commercial applications. It is used as a catalyst for hydrogenation or hydrodesulfurization reactions. Cobalt(II) sulfide is found in nature as the mineral sycoporite. The mineral linneite is made up of Co_3S_4 , tricobalt tetrasulfide.

Physical Properties

Cobalt(II) sulfide is reddish brown to black octahedral crystal; density 5.45 g/cm^3 ; melts above $1,100^\circ\text{C}$; practically insoluble in water (3.8 mg/L); slightly soluble in acids.

Cobalt(III) sulfide is a grayish-black crystalline substance; density 4.80 g/cm^3 ; insoluble in water; decomposes in acids.

Cobalt disulfide is a black cubic crystal; density 4.27 g/cm^3 ; insoluble in water; soluble in nitric acid.

Tricobalt tetrasulfide has a reddish color; density 4.86 g/cm^3 ; decomposes at 480°C ; insoluble in water.

Preparation

Cobalt sulfides are found in minerals, sycoporite and linneite, in different forms. Also, they may be readily prepared in the laboratory. A black precipitate of CoS is obtained by passing hydrogen sulfide through an alkaline solution of Co(II) salt, such as CoCl_2 . Also, the compound is produced by heating cobalt metal with H_2S at 700°C . Heating CoS with molten sulfur for a prolonged period yields cobalt disulfide, CoS_2 as a black powder. The disulfide may decompose and lose sulfur if heated at elevated temperatures.

Heating cobalt metal at 400°C with H_2S yields tricobalt tetrasulfide, Co_3S_4 . The temperatures must be well controlled in these preparative processes to obtain a specific sulfide. As the temperatures near 700°C the metal yields CoS , and above 700°C , it produces a sulfide that probably has the composition Co_9S_8 .

Analysis

The stoichiometric compositions may be determined from cobalt analysis of nitric acid extract of the solid material by AA, ICP, or other instruments. The structural form of sulfides and their composition may be analysed by x-ray diffraction or fluorescence methods.

TRICOBALT TETROXIDE

[1308-06-1]

Formula: Co_3O_4 ; MW 240.80

Synonyms: cobaltic cobaltous oxide; cobalto cobaltic oxide; cobaltosic oxide; tricobalt tetraoxide

Uses

Tricobalt tetroxide is a minor component of commercial cobalt oxides. It is used in ceramics, pigments, and enamels. Other applications are in grinding wheels, in semiconductors, and for preparing cobalt metal.

Physical Properties

Black cubic crystal; density 6.11 g/cm³; decomposes above 900°C, losing oxygen; insoluble in water; soluble in acids and alkalis

Thermochemical Properties

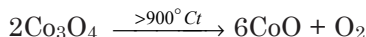
ΔH_f°	-212.95 kcal/mol
ΔG_f°	-184.99 kcal/mol
S°	24.5 cal/degree mol
C_p	29.5 cal/degree mol

Preparation

Tricobalt tetroxide is obtained when cobalt(II) carbonate, cobalt(II) or cobalt(III) oxide, or cobalt hydroxide oxide, $\text{CoO}(\text{OH})$ is heated in air at temperatures above 265°C. The temperature must not exceed 800°C (see decomposition temperature above).

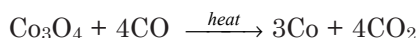
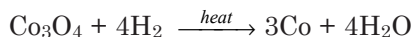
Reactions

Heating above 900°C expels oxygen out of the molecule forming cobalt(II) oxide:



Tricobalt tetroxide absorbs oxygen at lower temperatures, but there is no change in the crystal structure.)

The oxide is reduced to its metal by hydrogen, carbon or carbon monoxide.

**Analysis**

Elemental composition: Co 73.42%, O 26.58%. The nitric acid extract of the oxide may be analyzed for cobalt by various instrumental methods (see Cobalt). Additionally, the solid crystalline product may be characterized by x-ray techniques.

COPPER

[7440-50-8]

Symbol Cu; atomic number 29; atomic weight 63.546; a Group IB (Group 11) metal; electron configuration $[\text{Ar}]3d^{10}4s^1$; (electron configuration of Cu^+ , $[\text{Ar}]3d^{10}$ and Cu^{2+} $[\text{Ar}]3d^9$); most common valence states +1, +2; two natural isotopes, Cu-63 (69.09%), Cu-65 (30.91%).

Occurrence and Uses

The use of copper dates back to prehistoric times. The metal, its compounds, and alloys have numerous applications in every sphere of life—making it one of the most important metals. Practically all coinages in the world are made out of copper or its alloys. Its alloys, bronze and brass, date from ancient times. More modern alloys such as monel, gun metals, and beryllium-copper also have wide applications. The metal is an excellent conductor of electricity and heat and is used in electric wiring, switches and electrodes. Other applications are in plumbing, piping, roofing, cooking utensils, construction materials, and electroplated protective coatings. Its compounds, namely the oxides, sulfates, and chlorides, have numerous of commercial applications.

Copper is distributed widely in nature as sulfides, oxides, arsenides, arsenosulfides, and carbonates. It occurs in the minerals cuprite, chalcopyrite, azurite, chalcocite, malachite and bornite. Most copper minerals are sulfides or oxides. Native copper contains the metal in uncombined form. The principal copper minerals with their chemical compositions and percentage of copper are listed below:

chalcopyrite	CuFeS_2	34.5
chalcocite	Cu_2S	79.8
enargite	$\text{Cu}_3\text{As}_5\text{S}_4$	48.3
covellite	CuS	66.4
bornite	Cu_5FeS_4	63.3
azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	55.1
malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	57.3
cuprite	Cu_2O	88.8
tenorite	CuO	79.8
atacamite	$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$	59.4
tennantite	$\text{Cu}_3\text{As}_2\text{S}_7$	57.0
tetrahedrite	$\text{Cu}_8\text{Sb}_2\text{S}_7$	52.1
native copper	Cu	100

Physical Properties

Reddish brown metal; face-centered cubic crystal; density 8.92 g/cm³; Mohs hardness 2.5 to 3.0; Brinell hardness 43 (annealed); electrical resistivity 1.71 microhm-cm at 25°C; Poisson's ratio 0.33; melts at 1,083°C; vaporizes at 2,567°C; insoluble in water; dissolves in nitric acid and hot sulfuric acid; slightly soluble in hydrochloric acid; also soluble in ammonium hydroxide, ammonium carbonate and potassium cyanide solutions.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$S^\circ(\text{cry})$	7.92 cal/degree mol
$C_p(\text{cry})$	5.84 cal/degree mol
$\Delta H_f^\circ(\text{g})$	80.86 kcal/mol
$\Delta G_f^\circ(\text{g})$	71.37 kcal/mol
$S^\circ(\text{g})$	39.7 cal/degree mol
ΔH_{fus}	3.11 kcal/mol
Coeff. Linear expansion	$16.6 \times 10^{-6}/^\circ\text{C}$ at 25°C
Thermal conductivity	3.98 watts/cm $^\circ\text{C}$

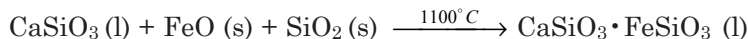
Production

In general, copper metal is extracted from its ores by various wet processes. These include leaching with dilute sulfuric acid or complexing with ligands (e.g., salicylaloximes), followed by solvent extraction. The solution is then electrolyzed to refine copper.

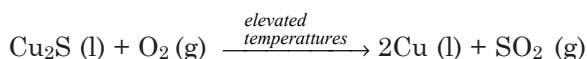
In most industrial processes, copper is produced from the ore chalcopyrite, a mixed copper-iron sulfide mineral, or from the carbonate ores azurite and malachite. The extraction process depends on the chemical compositions of the ore. The ore is crushed and copper is separated by flotation. It then is roasted at high temperatures to remove volatile impurities. In air, chalcopyrite is oxidized to iron(II) oxide and copper(II) oxide:



Then the roasted ore is combined with sand, powdered limestone, and some unroasted ore (containing copper(II) sulfide), and heated at $1,100^\circ\text{C}$ in a reverberatory furnace. Copper(II) sulfide is reduced to copper(I) sulfide. Calcium carbonate and silica react at this temperature to form calcium silicate, CaSiO_3 . The liquid melt of CaSiO_3 dissolves iron(II) oxide forming a molten slag of mixed silicate:



Lighter mixed silicate slag floats over the denser, molten copper(I) sulfide. Slag is drained off from time to time. Molten Cu_2S is transferred to a Bessemer converter where it is air oxidized at elevated temperatures producing metallic copper and sulfur dioxide:



Metallic copper obtained above is purified by electrolytic refining. The electrolytic cell consists of a cathode made of thin sheets of very pure copper connected to the negative terminal of a direct-current generator, and a lump of extracted impure copper from the ore serving as an anode. A solution of copper(II) sulfate in sulfuric acid is used as electrolyte. Electrolysis causes trans-

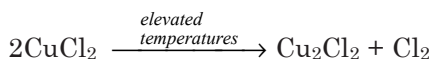
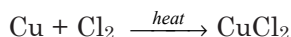
fer of copper from the anode to the electrolyte solution, and from there to the cathode. Pure copper is deposited on the cathode which grows longer and larger in size. The impure copper anode correspondingly becomes smaller and smaller in size. Also, a sludge, known as anode mud, collects under the anode. The mud contains ore impurities, such as silver, gold, and tellurium, which are more difficult to oxidize than copper. Copper-plating on other metals is done by similar methods.

Reactions

Copper forms practically all its stable compounds in +1 and +2 valence states. The metal oxidizes readily to +1 state in the presence of various complexing or precipitating reactants. However, in aqueous solutions +2 state is more stable than +1. Only in the presence of ammonia, cyanide ion, chloride ion, or some other complexing group in aqueous solution, is the +1 valence state (cuprous form) more stable than the +2 (cupric form). Water-soluble copper compounds are, therefore, mostly cupric unless complexing ions or molecules are present in the system. The conversion of cuprous to cupric state and metallic copper in aqueous media (ionic reaction, $2\text{Cu}^+ \rightarrow \text{Cu}^0 + \text{Cu}^{2+}$) has a K value of 1.2×10^6 at 25°C .

Heating the metal in dry air or oxygen yields black copper(II) oxide which on further heating at high temperatures converts to the red cuprous form, Cu_2O .

Copper combines with chlorine on heating forming copper(II) chloride. This dissociates into copper(I) chloride and chlorine when heated to elevated temperatures.



A similar reaction occurs with bromine; at first copper(II) bromide is formed which at red heat converts to copper(I) bromide. Fluorination yields CuF_2 . Heating the metal with iodine and concentrated hydriodic acid produces copper(I) iodide. When copper is heated in an atmosphere of hydrogen sulfide and hydrogen, the product is copper(I) sulfide, Cu_2S .

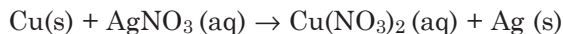
The standard electrode potentials, E° for the half-reactions are:



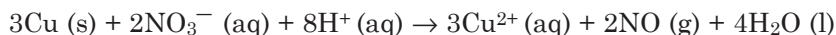
The metal is not strong enough to reduce H^+ from acids to H_2 . Therefore, under ordinary conditions, copper metal does not liberate hydrogen from mineral acids. Copper can reduce Ag^+ , Au^{3+} , and Hg^{2+} ions that have greater positive E° values for reduction half reactions, thus displacing these metals from their aqueous solutions.



Similarly, copper displaces silver from silver nitrate solution:



Copper liberates nitric oxide from nitric acid:



Copper(II) ion readily forms complexes with various ligands. It slowly forms a deep blue solution in aqueous ammonia. Its ammonia complex, $\text{Cu}(\text{NH}_3)_4^{2+}$ is very stable, the formation constant, K being 5.6×10^{11} .

Analysis

Copper may be analyzed readily at trace concentration levels by flame-AA, furnace-AA, ICP emission spectrophotometry, ICP-MS, neutron activation analysis, and the wavelength dispersive x-ray fluorescence method. Also, the metal may be determined by colorimetry. In colorimetric methods, aqueous solutions of copper salts are reduced to Cu^+ ions by hydroxylamine hydrochloride. The solution is treated with neocuproine (2,9-dimethyl-1,10-phenanthroline) to form a yellow complex or with bathocuproine (2,9-dimethyl-4,7,-diphenyl-1,10-phenanthroline) to form an orange product, the absorbance of which may be measured using a spectrophotometer or a filter photometer at 457 and 484 nm, respectively. The most sensitive wavelength for flame or furnace AA measurement is 324.7 nm. Suggested wavelengths for ICP measurement are 324.75 and 219.96 nm. ICP-MS offers a much lower detection limit than any other method. Copper imparts a deep green (parrot green) color to flame.

Toxicity

Although the toxicity of metallic copper is very low, many copper(II) salts may have varying degrees of toxicity. Inhalation of dusts, mists or fumes of the metal can cause nasal perforation, cough, dry throat, muscle ache, chills and metal fever. Copper in trace amounts is a nutritional requirement, used metabolically in plant and animal enzymes and other biological molecules. It can be either a toxicant or a nutrient within a concentration that may be in the same order of magnitude.

COPPER(II) ACETATE

[142-71-2]

Formula: $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$; MW 181.64; also forms a monohydrate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ [6046-93-1], MW 199.65.

Synonyms: cupric acetate; copper acetate; cupric diacetate; crystallized verdi-

gris; neutralized verdigris; crystals of Venus.

Uses

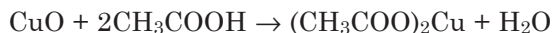
Copper(II) acetate is used as a pigment for ceramics; in the manufacture of Paris green; in textile dyeing; as a fungicide; and as a catalyst.

Physical Properties

Bluish-green fine powder; hygroscopic. The monohydrate is dimeric; density 1.88 g/cm³; melts at 115°C; decomposes at 240°C; soluble in water and ethanol; and slightly soluble in ether.

Preparation

Copper(II) acetate is prepared by treatment of copper(II) oxide, CuO, or copper(II) carbonate, CuCO₃, with acetic acid, followed by crystallization:



Analysis

Elemental composition: Cu 34.98%, C 26.45%, H 3.33%, O 35.24%. Copper(II) acetate is digested with nitric acid, diluted appropriately and analyzed for copper by various instrumental techniques (see Copper).

Toxicity

Copper(II) acetate is moderately toxic by ingestion and possibly other routes of administration.

LD₅₀ oral (rat): c. 600 mg/kg

COPPER ACETATE, BASIC

[52503-64-7]

Formula: Cu(C₂H₃O₂)₂·CuO·6H₂O; MW 369.27; the formula varies—several compositions are known at different ratios of copper acetate to copper oxide/hydroxide. The composition of blue verdigris is Cu(C₂H₃O₂)₂·CuO·5H₂O; green verdigris 2Cu(C₂H₃O₂)₂·CuO·5H₂O. Other compositions are Cu(C₂H₃O₂)₂·3CuO·2H₂O and Cu(C₂H₃O₂)₂·2CuO.

Synonyms: cupric acetate, basic; cupric subacetate

Uses

The basic copper acetate is used as a mordant in dyeing and printing; in the manufacture of Paris green and other pigments; and as a fungicide and insecticide.

Physical Properties

Color and form varies from blue crystals to greenish powder; slightly soluble in water and ethanol; soluble in dilute acids and ammonium hydroxide.

Preparation

The basic acetates are obtained by the treatment of copper with acetic acid followed by air oxidation.

Analysis

The compositions of the basic acetates with varying copper acetate-copper hydroxide-water ratios may be determined by elemental analyses of carbon, hydrogen, oxygen and copper. X-ray and thermogravimetric analyses should provide further information on their compositions.

COPPER(I) ACETYLIDE

[1117-94-8]

Formula: Cu_2C_2 ; MW 151.11

Structure: $\text{Cu}^+ \text{C}^- \equiv \text{C}^- \text{Cu}^+$

Synonyms: cuprous acetylide; cuprous carbide

Uses

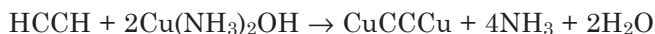
Copper(I) acetylide is used in a diagnostic test for CH unit; to prepare pure copper powder; in purification of acetylene; and as a catalyst in the synthesis of acrylonitrile and 2-propyn-1-ol.

Physical Properties

Red amorphous powder; explodes on heating; insoluble in water; soluble in acids.

Preparation

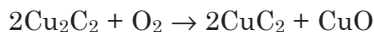
Copper(I) acetylide is prepared by passing acetylene gas over an aqueous solution of ammoniacal copper salt:



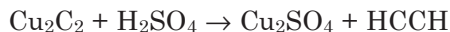
Also, the compound may be obtained by reacting acetylene with a soluble copper(I) salt solution.

Reactions

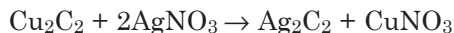
Copper(I) acetylide oxidizes in air forming copper(II) acetylide, CuC_2 :



Reactions with dilute mineral acids liberate acetylene and form the corresponding cuprous salts:



Copper(I) acetylide forms a highly explosive mixture containing silver acetylide when mixed with silver nitrate:

**Hazard**

In the dry state, the compound is highly sensitive to shock, exploding on impact. Also, it explodes when heated above 100°C. Spontaneous ignition occurs in chlorine, bromine or iodine vapors.

COPPER(II) ACETYLIDE

[12540-13-5]

Formula: CuC_2 ; MW 87.568

Structure: $(\text{CuCC})_n$

Synonyms: cupric acetylide; cupric carbide

Uses

Copper(II) acetylide is used as a detonator.

Physical Properties

Brownish black powder; insoluble in water.

Preparation

Copper(II) acetylide may be prepared by passing alkyl acetylene vapors over aqueous solution of ammoniacal copper salt.

Hazard

Copper(II) acetylide is highly sensitive to impact, friction or heat. Mild impact or heating can cause a violent explosion. In the dry state it is flammable and is more sensitive to impact or friction than copper(I) acetylide.

COPPER CARBONATE, BASIC

[12069-69-1]

Formula: $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$; MW 221.12

Synonyms: copper carbonate hydroxide; cupric carbonate basic; Bremen green; Bremen blue; mineral green.

Uses

Basic copper carbonate is used as a pigment in paint and varnish; as a fungicide for seed treatment; as an insecticide; in pyrotechnics; and in the manufacture of other copper salts. The compound is also added in small quantities to animal and poultry feed to supply nutritional copper requirements.

Basic copper carbonate occurs in nature as minerals, malachite and azurite. While the carbonate to hydroxide molar composition ratio in natural malachite is 1:1, the ratio in azurite $[2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2]$ is 2:1.

Physical Properties

Natural malachite is a dark green crystalline solid; monoclinic crystals; density 4.0 g/cm^3 ; refractive index 1.655; decomposes at 200°C ; insoluble in cold water and alcohols; decomposes in hot water; soluble in acids, ammonium hydroxide and potassium cyanide solutions.

Natural azurite is blue monoclinic crystal; density 3.88 g/cm^3 ; refractive index 1.730; decomposes at 220°C ; insoluble in cold water; decomposes in hot water; soluble in ammonium hydroxide and hot sodium bicarbonate solutions.

Preparation

Basic carbonate is obtained from its naturally occurring minerals. It also may be prepared by mixing a solution of copper sulfate with sodium carbonate. The precipitate is then filtered and dried.

Analysis

Elemental composition: Cu 57.47%, C 5.43%, H 0.91%, O 36.18%. Both malachite and azurite may be identified by x-ray analysis and analyzed qualitatively using physical properties such as refractive index and density. For quantitative analysis, the compound may be digested in nitric acid and analyzed for copper by various instrumental methods (see Copper.)

COPPER(I) CHLORIDE

[7758-89-6]

Formula: CuCl (dimeric, Cu_2Cl_2 , in vapor state); MW 98.99; zinc blende structure consisting of tetrahedrally coordinated Cu^+ ; Cu—Cl bond length $2.16\text{\AA}$.
Synonym: cuprous chloride

Uses

Copper(I) chloride is used as a catalyst in the production of chlorine by oxygenation of hydrogen chloride. Other important applications are in the petroleum industry as a desulfurization and decolorizing agent; as a condensing agent for fats and oils; as a fungicide; and as an absorbent for carbon monoxide in gas analysis. It occurs in nature as mineral nantokite.

Physical Properties

White cubic crystal which turns blue when heated at 178°C ; density 4.14 g/cm^3 ; the mineral nantokite (CuCl) has density 4.14 g/cm^3 , hardness 2.5 (Mohs), refractive index 1.930; melts at 430°C becoming a deep, green liquid; vaporizes around $1,400^\circ\text{C}$; vapor pressure 5 torr at 645°C and 400 torr at $1,250^\circ\text{C}$; low solubility in water (decomposes partially); $K_{\text{sp}} 1.72 \times 10^{-7}$; insoluble in ethanol and acetone; soluble in concentrated HCl and ammonium hydroxide.

Thermochemical Properties

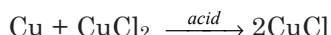
ΔH_f°	-32.79 kcal/mol
ΔG_f°	-28.66 kcal/mol
S°	20.60 cal/degree mol
C_p	11.59 cal/degree mol
ΔH_{fus}	2.438 kcal/mol

Preparation

Copper(I) chloride is prepared by reduction of copper(II) chloride in solution:



Alternatively, it can be prepared by boiling an acidic solution of copper(II) chloride with copper metal, which on dilution yields white CuCl:



Copper(I) chloride dissolved in concentrated HCl absorbs carbon monoxide under pressure forming an adduct, $\text{CuCl}(\text{CO})$. The complex decomposes on heating releasing CO.

Copper(I) chloride is slightly soluble in water. However, in the presence of Cl^- ion, it forms soluble complexes of discrete halogeno anions such as, CuCl_2^- , CuCl_3^{2-} , and CuCl_4^{3-} .

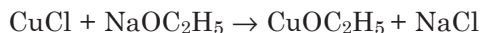
Formation of complexes and organocopper derivatives as outlined below are not confined only to copper(I) chloride, but typify Cu^+ in general.

Reaction with ethylenediamine (en) in aqueous potassium chloride solution forms Cu(II)-ethylenediamine complex, while Cu^+ ion is reduced to its metallic state:



It dissolves in acetonitrile, CH_3CN forming tetrahedral complex ion $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ which can be precipitated with large anions such as ClO_4^- or PF_6^- .

Reactions with alkoxides of alkali metals produce yellow copper(I) alkoxides. For example, reaction with sodium ethoxide yield copper(I) ethoxide, a yellow compound that can be sublimed from the product mixture:



Copper(I) chloride forms complexes with ethylene and other alkenes in solutions that may have compositions such as $[\text{Cu}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2]^+$ or $[\text{Cu}(\text{C}_2\text{H}_4)(\text{bipy})]^+$. (bipy = bipyridyl)

Reactions with lithium or Grignard reagent yield alkyl or aryl copper(I) derivatives, respectively. Such organocopper compounds containing Cu-Cu bonds are formed only by Cu^+ and not Cu^{2+} ions.

Analysis

Elemental composition: Cu 64.18%, Cl 35.82%. Copper(I) chloride is dissolved in nitric acid, diluted appropriately and analyzed for copper by AA or ICP techniques or determined nondestructively by X-ray techniques (see Copper). For chloride analysis, a small amount of powdered material is dissolved in water and the aqueous solution titrated against a standard solution of silver nitrate using potassium chromate indicator. Alternatively, chloride ion in aqueous solution may be analyzed by ion chromatography or chloride ion-selective electrode. Although the compound is only sparingly soluble in water, detection limits in these analyses are in low ppm levels, and, therefore, dissolving 100 mg in a liter of water should be adequate to carry out all analyses.

Toxicity

Copper(I) chloride is moderately toxic by ingestion and possibly other routes of entry into the body. The oral LD₅₀ in mouse is reported to be 347 mg/kg; and subcutaneous LD₅₀ in guinea pigs is 100 mg/kg.

COPPER(II) CHLORIDE

[7447-39-4]

Formula: CuCl_2 ; MW 134.45; forms a dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ [10125-13-0]
MW 170.48

Synonyms: cupric chloride; cupric dichloride

Uses

Copper(II) chloride is used as a mordant in dyeing and printing of fabrics; as an ingredient of isomerization and cracking catalysts; and as a desulfurizing and deodorizing agent in petroleum industry. Other important applications are in copper plating of aluminum; in tinting-baths for iron and tin; in pigments for ceramics and glasses; as a fixer and desensitizer reagent in photography; in mercury extraction from ores; in laundry-marking and invisible inks; and in manufacture of several copper salts.

Physical Properties

The anhydrous form constitutes yellow to brown monoclinic crystals. It is hygroscopic; forms dihydrate on exposure to moist air; density 3.40 g/cm³; melts around 630°C with decomposition; soluble in water, ethanol and acetone.

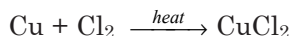
The dihydrate exists as greenish blue orthorhombic crystals; density 2.51 g/cm³; decomposes at 100°C; is very soluble in water and ethanol (solubility greater than anhydrous salt in these solvents); also soluble in acetone; insoluble in ether.

Thermochemical Properties

ΔH_f°	-52.61 kcal/mol
ΔG_f°	-41.99 kcal/mol
S°	25.84 cal/degree mol
C_p	17.18 cal/degree mol
ΔH_{fus}	4.88 kcal/mol

Preparation

Copper(II) chloride may be synthesized by heating elemental copper with chlorine:



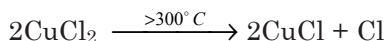
Alternatively, it may be prepared by treating copper carbonate with hydrochloric acid followed by crystallization:



In the above preparation, the hydrate of the salt crystallizes, precipitates, and may be dehydrated by heating under vacuum.

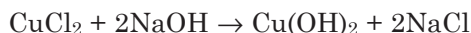
Reactions

When heated above 300°C, copper(II) chloride partially decomposes to copper(I) chloride and chlorine:



Also, it is reduced to CuCl and elemental copper when treated with reducing agents.

Fluorination with fluorine produces copper(II) fluoride, CuF₂. Adding potassium ferrocyanide to CuCl₂ aqueous solution precipitates out reddish brown cupric ferrocyanide. Reaction with caustic soda forms blue cupric hydroxide:



Black copper(II) sulfide, CuS, is obtained when hydrogen sulfide is passed through dissolved CuCl₂.

CuCl₂ forms several copper(II) complexes with several types of ligands in aqueous solutions.

Analysis

Elemental composition: Cu 47.26%, Cl 52.74%. Aqueous CuCl₂ may be analyzed for copper by various instrumental methods (see Copper) and the chloride anion may be analyzed by ion chromatography, chloride ion-selective electrode, or by titration with a standard solution of silver nitrate.

COPPER(II) CHROMATE

[13548-42-0]

Formula: CuCrO_4 ; MW 179.54; several basic copper chromates are known in combination with copper(II) hydroxide at varying ratios of CuCrO_4 to $\text{Cu}(\text{OH})_2$; $\text{CuCrO}_4 \cdot \text{Cu}(\text{OH})_2$, $\text{CuCrO}_4 \cdot 2\text{Cu}(\text{OH})_2$, and $2\text{CuCrO}_4 \cdot 3\text{Cu}(\text{OH})_2$. Their colors vary.

Synonyms: neutral cupric chromate; copper chromate neutral

Uses

The neutral and basic forms of copper(II) chromate are used as mordants in dyeing textiles; as fungicides; to protect textiles from damage by microorganisms and insects; and as wood preservatives.

Physical Properties

The neutral form is a reddish-brown crystalline solid; decomposes slowly to copper(II) chromite when heated above 400°C ; insoluble in water; soluble in acids.

The basic chromates are crystals having colors that vary from yellow to chocolate-brown to lilac, depending on their compositions and chromate to hydroxide molar ratios. They lose water when heated at 260°C , are insoluble in water, and are soluble in nitric acid.

Preparation

Neutral copper(II) chromate may be prepared by treating copper(II) carbonate, CuCO_3 , with aqueous solutions of sodium chromate, Na_2CrO_4 and chromium(VI) oxide, CrO_3 .

Basic copper(II) chromate may be obtained by treating copper(II) hydroxide, $\text{Cu}(\text{OH})_2$ with an aqueous solution of chromium(VI) oxide.

Analysis

Elemental composition (neutral CuCrO_4): Cu 35.39%, Cr 28.97%, O 35.64%. These chromates are analyzed by x-ray, thermogravimetric analysis (the basic form loses water around 260°C) and metal analysis. Copper and chromium may be analyzed by digesting the compound(s) with nitric acid, diluting appropriately with water, followed by AA, ICP, or other instrumental analysis. (see Chromium and Copper).

COPPER(II) CHROMITE

[12018-10-9]

Formula: CuCr_2O_4 ; MW 231.54

Synonyms: cupric chromite; cupric chromate(III)

Uses

Copper(II) chromite or its mixture with copper(II) oxide is used as a cata-

lyst for selective hydrogenation of olefinic double bonds; or for the hydrogenolysis of methyl esters of fatty acids (at high temperatures and pressures) to produce fatty alcohols.

Physical Properties

Grayish-black tetragonal crystals; density 5.4 g/cm³. When heated to elevated temperatures (above 900°C) copper(II) chromite decomposes to cupric chromate(II), CuCrO₂ and chromium (VI) oxide, CrO₃. Copper(II) chromite is insoluble in water and dilute acids.

Preparation

Copper(II) chromite is obtained by heating copper chromate, CuCrO₄ at 400°C. The Adkin catalyst, a mixture of copper oxide and copper chromite, is prepared by mixing aqueous solutions of copper nitrate, sodium dichromate and ammonium hydroxide; the orange precipitate of copper ammonium chromate formed is dried and then heated below 400°C.

Analysis

The elemental composition of CuCr₂O₄: Cu 27.44%, Cr 44.92%, O 27.64%.

The catalyst is analysed by measurement of surface area and pore volume; also by differential thermal analysis, thermogravimetric analysis and x-ray studies.

COPPER(I) CYANIDE

[544-92-3]

Formula: CuCN; MW 89.564

Synonyms: cuprous cyanide; cupricin

Uses

Copper(I) cyanide is used in copper plating of nickel, chromium, zinc alloys, steel, and other metals or alloys. Such copper plating imparts brightness, smoothness, hardness, and strength. The cyanide solution employed for copper electroplating consists of copper cyanide and sodium cyanide. Other applications of this compound are as an insecticide, a catalyst in polymerization, and as an antifouling agent in marine paints.

Physical Properties

Cream-colored powder or green orthorhombic or red monoclinic crystals; density 2.90 g/cm³; melts at 474°C; decomposes at higher temperatures; practically insoluble in water, ethanol, and cold dilute acids; dissolves in ammonium hydroxide and potassium cyanide solutions.

Preparation

Copper(I) cyanide is a precipitate obtained by adding potassium cyanide solution to an aqueous solution of Cu²⁺ salt:



The Cu^{2+} to CN^- molar ratio should be 1:2. The precipitate dissolves in an excess of cyanide, forming soluble ions $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$, and $\text{Cu}(\text{CN})_4^{3-}$.

Analysis

Elemental composition: Cu 70.95%, C 13.41%, N 15.64%. Copper(I) cyanide is decomposed in nitric acid and the acid extract diluted appropriately and analyzed for copper by various instrumental methods (see Copper).

Toxicity

The compound is a poison by ingestion and other routes of exposure.

COPPER(II) FLUORIDE

[7789-19-7]

Formula: CuF_2 ; MW 101.54; also forms a dihydrate, $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ [13454-88-1], MW 137.57

Synonym: cupric fluoride

Uses

Copper(II) fluoride is used in cathodes in nonaqueous galvanic cells, such as high energy batteries. It also is used as a fluorinating agent. The dihydrate is used in welding and brazing fluxes and is added to cast iron to improve its strength. Another application of this compound is as opacifier in ceramics, glasses and enamels.

Physical Properties

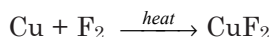
The anhydrous fluoride is a white crystalline solid; monoclinic crystals; turns blue in moist air; density 4.23 g/cm³; melts at 836°C; vaporizes at 1,676°C; sparingly soluble in water (hydrolyzes in hot water). The dihydrate is blue monoclinic crystal; density 2.934 g/cm³; decomposes at 130°C; slightly soluble in water.

Thermochemical Properties

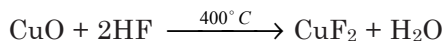
ΔH_f°	-129.71 kcal/mol
ΔH_{fus}	13.15 kcal/mol

Preparation

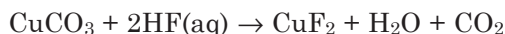
Copper(II) fluoride is prepared by direct fluorination of copper at high temperatures:



It also may be prepared by passing hydrogen fluoride gas over copper(II) oxide at 400°C:

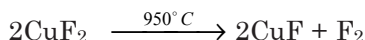


Alternatively, it may be made by treating copper carbonate with hydrofluoric acid followed by crystallization.



Reactions

Copper(II) fluoride loses fluorine as it melts. At 950°C it converts to copper(I) fluoride (cuprous fluoride), CuF :



Also, when it is heated at 1,200°C in an atmosphere of hydrogen fluoride, copper(I) fluoride is produced.

Reaction with water is slow, forming a hydrate. The product decomposes slowly at ambient temperature with liberating hydrogen fluoride, leaving a basic fluoride, CuFOH . The dihydrate hydrolyzes to oxyfluoride $\text{Cu}(\text{OF})_2$ in hot water.

Analysis

Elemental composition: Cu 62.58%, F 37.42%. Copper(II) fluoride acid extract is analyzed for copper by instrumental methods. Powder may be analyzed by the x-ray diffraction method. Aqueous solution (in cold water) may be analyzed for fluoride ion using a fluoride ion-selective electrode or by ion chromatography.

Toxicity

Copper(II) fluoride is moderately toxic by ingestion and other routes of exposure.

COPPER(II) HYDROXIDE

[20427-59-2]

Formula: $\text{Cu}(\text{OH})_2$; MW 97.56

Synonyms: cupric hydroxide; copper hydrate; hydrated copper oxide

Uses

Copper(II) hydroxide is used as a mordant in pigments; for staining paper; as an additive to cattle feed; as a catalyst; as a fungicide; and in the preparation of several copper salts.

Physical Properties

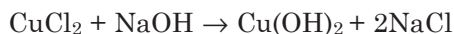
Blue crystalline powder or gelatinous mass; density 3.36 g/cm³; decomposes on heating; insoluble in cold water; K_{sp} 2.20×10^{-20} ; decomposes in hot water; soluble in acids, ammonium hydroxide and potassium cyanide.

Thermochemical Properties

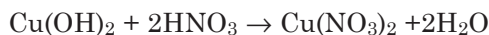
ΔH_f° (cry)	-107.5 kcal/mol
ΔH_f° (aq)	-94.46 kcal/mol
ΔG_f° (aq)	-59.53 kcal/mol

Preparation

Copper(II) hydroxide is precipitated by treating a soluble copper(II) salt such as, CuCl₂ or CuSO₄ with caustic soda or caustic potash:

**Reactions**

Thermal decomposition yields copper(II) oxide. Reactions with mineral acids yield the corresponding copper(II) salts:



Copper(II) hydroxide dissolves in concentrated alkali hydroxides forming deep blue anions of [Cu(OH)₄]²⁻ and [Cu(OH)₆]⁴⁻.

Reaction with hydrofluosilicic acid followed by crystallization yields blue crystals of hydrated cupric fluosilicate, CuSiF₆·4H₂O.

When heated with abietic acid, the product is a green salt, cupric abietate, Cu(C₂₀H₂₉O₂)₂, a metal paint and fungicide.

Analysis

Elemental composition: Cu 65.13%, H 2.07%, O 32.80%

Copper is determined by AA or ICP spectrophotometry of copper(II) hydroxide nitric acid extract. Heating the solid hydroxide dehydrates to CuO. The moles of water loss may be measured by gravimetric analysis. The black CuO residue may be identified by x-ray analysis and physical tests.

Toxicity

Copper(II) hydroxide is low to moderately toxic by ingestion. LD₅₀ oral (rat): 1,000 mg/kg.

COPPER(I) IODIDE

[7681-65-4]

Formula: CuI; MW 190.45

Synonym: cuprous iodide

Uses

The iodide salt is used as a source of dietary iodine in table salt and animal feed; in cloud seeding; as a coating in cathode ray tubes; as a temperature indicator; and as a catalyst in organic reactions.

Copper(I) iodide is found in nature as mineral marshite.

Physical Properties

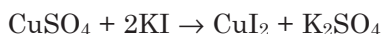
White powder; cubic crystals; the mineral marshite is a red-brown crystal; density 5.67 g/cm³; refractive index 2.346; hardness 2.5 Mohs; melts at 606°C; vaporizes around 1,290°C; insoluble in water and dilute acids; soluble in aqueous solutions of ammonia and alkali salts of cyanide, iodide and thiosulfate ions.

Thermochemical Properties

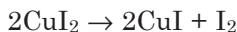
ΔH_f°	-16.20 kcal/mol
ΔG_f°	-16.61 kcal/mol
S°	23.11 cal/degree mol
C_p	12.93 cal/degree mol

Preparation

Copper(I) iodide is prepared by heating copper with iodine and concentrate hydriodic acid, HI. Another preparation route is precipitation of the salt by mixing aqueous solutions of potassium or sodium iodide with copper sulfate or any soluble copper(II) salt:



The unstable CuI₂ formed rapidly dissociates into insoluble copper(I) iodide and iodine



Analysis

Elemental composition: Cu 33.36%, I 66.64%. Either compound or mineral copper(I) iodide is identified by x-ray diffraction or fluorescence method. Copper may be analyzed in nitric acid extract of copper(I) iodide by various instrumental techniques (see Copper).

COPPER(II) NITRATE

[3251-23-8]

Formula: Cu(NO₃)₂; MW 187.56; two hydrates are known, namely, copper nitrate trihydrate Cu(NO₃)₂•3H₂O [10031-43-3], MW 241.60 and copper nitrate hexahydrate, Cu(NO₃)₂•6H₂O [13478-38-1] MW 295.65.

Synonyms: cupric nitrate; copper dinitrate

Uses

Copper(II) nitrate is used in light-sensitive reproduction papers; as a mordant in dyeing and printing of fabrics; as a coloring reagent for ceramics; for coloring copper black; as a burnishing agent for iron; in nickel-plating baths; in pyrotechnic compositions; and in paints, varnishes, and enamels. Other applications are as an oxidizing agent; nitrating agent for aromatics; as a catalyst; and an analytical standard for copper.

Copper nitrate trihydrate occurs in nature as the mineral gerhardite.

Physical Properties

Blue-green orthorhombic crystals; deliquescent; density 2.05 g/cm³; melts at 255°C; sublimes; readily dissolves in water, alcohols and dioxane.

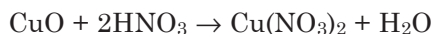
The trihydrate and hexahydrate are blue rhombohedral crystals; hygroscopic; density 2.32 g/cm³ (trihydrate), 2.07 g/cm³ (hexahydrate); melts at 114°C (trihydrate); trihydrate decomposes at 170°C; hexahydrate decomposes to trihydrate at 26.4°C; both the hydrates are very soluble in water and ethanol.

Thermochemical Properties

$$\Delta H_f^\circ \quad -72.39 \text{ kcal/mol}$$

Preparation

Copper(II) nitrate is made by action of copper or copper(II) oxide with nitric acid. The solution is evaporated and the product is obtained by crystallization



The nitrate salt prepared by this method is hydrated. It cannot be dehydrated fully without decomposition. Anhydrous CuNO₃ may be prepared by dissolving copper metal in a solution of dinitrogen tetroxide, N₂O₄, in ethyl acetate. Upon crystallization, an N₂O₄ adduct of Cu(NO₃)₂ that probably has the composition [NO⁺][Cu(NO₃)₃] is obtained. This adduct, on heating at 90°C, yields blue anhydrous copper(II) nitrate which can be sublimed in vacuum at 150°C and collected.

Reactions

Thermal decomposition of copper(II) nitrate produces copper oxides and nitrogen oxides.

In aqueous solutions, copper(II) nitrate undergoes many double decomposition reactions with soluble salts of other metals, forming precipitates of insoluble copper salts.

When H₂S is passed through its aqueous solution, black CuS precipitates.

Copper(II) nitrate reacts with ether forming a complex.

Analysis

Elemental composition: Cu 33.88%, N 14.94%, O 51.18%. Copper(II) nitrate aqueous solution with appropriate dilution may be analyzed for copper by var-

ious instrumental methods (see Copper). After appropriate dilution, the nitrate anion in the aqueous solution may be measured by ion chromatography or nitrate ion-selective electrode.

Hazard

Copper(II) nitrate is moderately toxic by ingestion. Skin or eye contact can cause irritation.

LD₅₀ oral (rat): 940 mg/kg.

Copper(II) nitrate, being an oxidizing agent, can undergo violent reactions with readily oxidizable substances. Reaction with acetic anhydride is violent, and heating with potassium or ammonium ferrocyanide at 220°C may cause an explosion. It can ignite paper on prolonged contact.

COPPER(I) OXIDE

[1317-39-1]

Formula: Cu₂O; MW 143.09

Synonyms: cuprous oxide; copper suboxide; copper oxide red; copper protoxide; copper hemioxide

Uses

An important application of copper(I) oxide is in antifouling paints for steel, wood, and other materials exposed to sea water. Other applications include manufacture of ruby-red glass and preparation of miscellaneous copper salts. It also is used as a reducing agent in brazing pastes; as a fungicide; in photocells; and as a catalyst.

Copper(I) oxide occurs in nature as the mineral cuprite.

Physical Properties

Reddish-brown cubic crystals; density 6.0 g/cm³; Mohs hardness 3.8; melts at 1,235°C; decomposes around 1,800°C; insoluble in water; soluble in ammonium hydroxide.

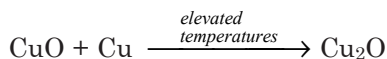
Thermochemical Properties

ΔH_f°	-40.30 kcal/mol
ΔG_f°	-34.89 kcal/mol
S°	22.25 cal/degree mol
C_p	15.20 cal/degree mol

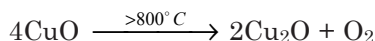
Preparation

Copper(I) oxide is found in nature as the mineral cuprite. Copper(I) oxide can be prepared by several methods, which include:

(1) Reduction of a copper(II) oxide with copper at elevated temperatures in a furnace:



(2) Thermal decomposition of copper(II) oxide:



(at elevated temperatures Cu_2O is more stable than CuO)

(3) Controlled reduction of an alkaline solution of a Cu^{2+} salt with hydrazine, N_2H_4 . In this method, Cu_2O is produced as a yellow powder.

(4) Oxidation of finely divided copper.

(5) Thermal decomposition of copper ammonium carbonate:



(6) Reaction of alkali hydroxide with copper(I) chloride:

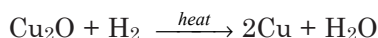


(7) Reduction of copper(II) hydroxide, $\text{Cu}(\text{OH})_2$ with sulfur dioxide, glucose, or another reducing agent.

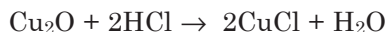
(8) Electrolyzing an aqueous solution of NaCl using copper electrodes. The technical grade product should contain minimum 97% Cu_2O for use in pigments.

Reactions

Oxidation produces copper(II) oxide, CuO . Heating with hydrogen reduces the oxide to metallic copper:



The oxide reacts with HCl forming CuCl :

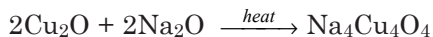


CuCl dissolves in excess HCl .

Copper oxide reacts with dilute sulfuric and nitric acids forming copper(II) sulfate and copper(II) nitrate, respectively, and precipitating metallic copper:



Heating with alkali metal oxides such as Na_2O and K_2O produces alkali metal oxocuprates that have the compositions $\text{Na}_4\text{Cu}_4\text{O}_4$ or $\text{K}_4\text{Cu}_4\text{O}_4$ containing oxocuprate, $[\text{Cu}_4\text{O}_4]^{4-}$ rings:



Reaction with trifluoromethanesulfonic anhydride in benzene yields copper(I) trifluoromethanesulfonate, $[\text{Cu}(\text{O}_3\text{SCF}_3)]_2 \cdot \text{C}_6\text{H}_5$, a white crystalline, air-sensitive complex (Cotton, F. A., G. Wilkinson, C. A. Murillo and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. pp. 857-858. New York: Wiley Interscience) Olefins can displace benzene in the above compound readily, forming a variety of olefin complexes.

Analysis

Elemental composition: Cu 88.42%, O 11.18%. The oxide may be dissolved in excess hydrochloric acid, diluted appropriately and analyzed by AA or ICP techniques (see Copper). The mineral cuprite may be identified nondestructively by various x-ray methods.

Hazard

Copper(I) oxide is moderately toxic by ingestion.

LD₅₀ oral (rat): 470 mg/kg

Violent reaction can occur when copper(I) oxide is heated with aluminum

COPPER(II) OXIDE

[1317-38-0]

Formula: CuO; MW 79.545

Synonyms: cupric oxide; copper oxide black

Uses

Copper(II) oxide is used as pigments for coloring glass, ceramics, porcelain and artificial gems; in batteries and electrodes; in antifouling paints; in electroplating; in welding fluxes for bronze; in the production of rayons; for removal of sulfur from oils; in phosphor mixtures; for polishing optical glass; and as a catalyst. It also is used to prepare various copper compounds.

Copper(II) oxide is found in nature as the minerals tenorite and paramelaconite. They differ in crystalline structure: tenorite exists as triclinic crystals while paramelaconite consists of tetrahedral cubic crystals.

Physical Properties

Black powder or monoclinic crystals; density 6.31 g/cm³; melts at 1,446°C; insoluble in water and alcohols; soluble in dilute acids and ammonium hydroxide.

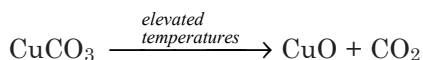
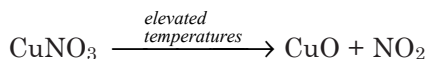
Thermochemical Properties

ΔH_f°	-37.60 kcal/mol
ΔG_f°	-31.00 kcal/mol
S°	10.18 cal/degree mol

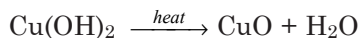
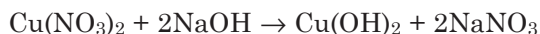
C_p	10.11 cal/degree mol
ΔH_{fus}	2.82 kcal/mol

Preparation

Copper(II) oxide occurs in nature as the mineral tenorite. It may be prepared by pyrolysis of copper nitrate, copper carbonate or another oxo copper salt

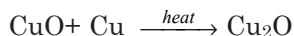


Also, copper(II) oxide may be prepared by adding alkali hydroxide to a cupric salt solution; the bulky blue slurry of hydroxide obtained is then dehydrated by warming:



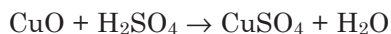
Reactions

Heating above 800°C converts copper(II) oxide into copper(I) oxide. Also, when the black oxide is heated with copper metal, copper(I) oxide is formed:



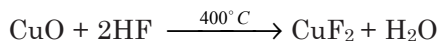
Copper(II) oxide reacts with dilute sulfuric acid and nitric acid forming copper(II) sulfate and copper(II) nitrate, respectively.

These salts are obtained following evaporation of the solution and crystallization:



The oxide is reduced to metallic copper when heated at high temperatures with hydrogen and other reducing agents.

Heating with hydrogen fluoride at 400°C yields copper(II) fluoride, CuF_2 :



Analysis

Elemental composition: Cu 79.88%, O 20.12%. Copper(II) oxide is dissolved in nitric or sulfuric acid and copper content may be determined by AA or ICP spectrometry following appropriate dilution of the acid extract. It may be alternatively analyzed nondestructively by x-ray methods.

COPPER(II) SULFATE

[7758-98-7]

Formula: CuSO_4 ; MW 159.61; also exists as a pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [7758-99-8], MW 249.69

Synonyms: cupric sulfate; blue vitriol; blue copperas; blue stone

Uses

Copper(II) sulfate is probably the most important of all copper compounds. It is used extensively in agriculture as a soil additive to improve crop yields. Other applications are as a feed additive to prevent copper deficiency; a mordant in textiles; in pigments; in electric batteries; in copper plating; as a fungicide (such as Bordeaux mixture); as a wood preservative; in lithography and process engraving; in medicine; as a dehydrating agent (anhydrous salt); and in the manufacture of other copper compounds.

The pentahydrate occurs in nature as the mineral, chalcantite; the anhydrous sulfate occurs as mineral, hydrocyanite.

Physical Properties

The anhydrous salt is greenish-white rhombohedral crystals or amorphous powder; hygroscopic; density 3.60 g/cm^3 ; decomposes above 560°C ; soluble in water; insoluble in ethanol.

The pentahydrate is large blue triclinic crystal or light-blue amorphous powder; refractive index 1.514; density 2.28 g/cm^3 ; loses water on heating—two molecules at 30°C , becomes a monohydrate at 110°C and anhydrous at 250°C ; very soluble in water; moderately soluble in methanol; slightly soluble in ethanol.

Thermochemical Properties

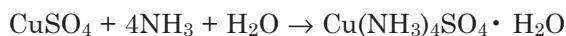
ΔH_f°	-184.37 kcal/mol
ΔG_f°	-158.27 kcal/mol
S°	$26.1 \text{ cal/degree mol}$

Reactions

Thermal decomposition of copper(II) sulfate produces copper(II) oxide and sulfur trioxide.

When heated with rosin oil, a green precipitate of copper(II) resinate is obtained. Similarly, with sodium stearate, $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}$, and sodium oleate, $\text{C}_{18}\text{H}_{33}\text{O}_2\text{Na}$, it precipitates as light blue cupric stearate, $(\text{C}_{18}\text{H}_{35}\text{O}_2)_2\text{Cu}$ and greenish-blue copper oleate $\text{Cu}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$, respectively. It forms copper carbonate, basic $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and basic copper sulfate (varying compositions) with sodium carbonate. With caustic soda, the reaction product is copper(II) hydroxide, $\text{Cu}(\text{OH})_2$.

When dissolved in ammonium hydroxide and treated with ethanol dark blue complex, copper amino sulfate is obtained:



Reaction with oxalic acid produces bluish-white copper(II) oxalate, CuC_2O_4 .

When mixed with a solution of borax a blue-green solid of indefinite composition, copper(II) borate, precipitates.

Reaction with potassium cyanide yields green copper(II) cyanide, $\text{Cu}(\text{CN})_2$.

Analysis

Elemental composition (CuSO_4): Cu 39.81%, S 20.09%, O 40.10%. Aqueous solution of copper(II) sulfate may be analyzed for copper by instrumental techniques (see Copper). The sulfate anion may be determined by ion chromatography. The crystal may be characterized by x-ray techniques and other physical tests.

Toxicity

Copper(II) sulfate is toxic to humans by ingestion and other routes of exposure. Symptoms of ingestion include gastritis, diarrhea, nausea, vomiting, kidney damage and hemolysis (Lewis (Sr.), R. N. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

LD₅₀ oral (rat): 300 mg/kg

COPPER(II) SULFATE, BASIC

[1332-14-5]

Occurrence and Uses

The formula varies; several salts with variable compositions of CuSO_4 and $\text{Cu}(\text{OH})_2$ or CuO are known. Some of them occur in nature as minerals:

Copper hydroxide sulfate or cupric subsulfate is found in nature as the mineral dolerophane; formula: $\text{CuSO}_4 \cdot \text{CuO}$

Copper sulfate dibasic occurs in nature as mineral antlerite; formula: $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$

Copper sulfate tribasic occurs in nature as mineral brochantite; formula: $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$

Copper sulfate tribasic hydrate is also found in nature as mineral langite; formula: $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$

These basic salts of copper(II) sulfate are light-to-deep blue crystals of fine particle size; density in the range 3.5 to 4.0 g/cm³; practically insoluble in water; dissolve in acids. They may be prepared by various methods depending on the nature of the product desired; i.e., mixing solutions of CuSO_4 and Na_2CO_3 yields Burgundy mixtures, or CuSO_4 with $\text{Ca}(\text{OH})_2$ yields Bordeaux mixture.

Basic copper sulfate salts are used as fungicides for plants.

COPPER(I) SULFIDE

[22205-45-4]

Formula: Cu_2S ; MW 159.16; slightly copper deficient, the probable composition $\text{Cu}_{1.8}\text{S}$

Synonym: cuprous sulfide

Uses

Copper(I) sulfide is used in luminous paints; antifouling paints; in solid-lubricant mixtures; in solar cells; in electrodes; and as a catalyst.

The compound occurs in nature as the mineral chalcocite (copper glance) with varying colors.

Physical Properties

Dark-blue or black orthogonal crystals; density 5.6 g/cm³; hardness 2.8 Mohs; melts at about 1,100°C; insoluble in water; slightly soluble in hydrochloric acid; decomposed by nitric acid and concentrated sulfuric acid; moderately soluble in ammonium hydroxide; dissolves in potassium cyanide solutions.

Thermochemical Properties

ΔH_f°	-19.00 kcal/mol
ΔG_f°	-20.60 kcal/mol
S°	28.90 cal/degree mol
C_p	18.24 cal/degree mol

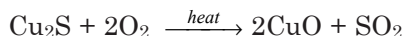
Preparation

Copper(I) sulfide is available in nature as the mineral chalcocite. It also may be made by heating copper(II) sulfide with hydrogen, in the presence of small amounts of sulfur.

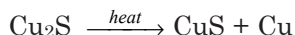
Alternatively, copper(I) sulfide may be prepared by heating copper with hydrogen sulfide and hydrogen; or by heating the metal with sulfur in an atmosphere of carbon dioxide and methanol vapor.

Reactions

When heated in air, copper(I) sulfide oxidizes forming copper(II) oxide, and sulfur dioxide:



Heating in the absence of air produces copper(II) sulfide and copper:



When heated with nitric acid, copper(I) sulfide decomposes forming copper nitrate and hydrogen sulfide. The compound dissolves in aqueous solutions containing cyanide ions forming soluble copper-cyanide complexes.

Copper(I) sulfide reacts with polysulfide anions in aqueous solutions forming soluble copper polysulfides.

Analysis

Elemental composition: Cu 79.85%, S 20.15%.

Copper(I) sulfide may be analyzed by x-ray analyses. The copper concentration in nitric acid extract may be measured by various instrumental techniques (see Copper).

COPPER(II) SULFIDE

Formula: CuS ; MW 95.61; structurally complex, the compound probably consists of S_2^{-2} and S^{-2} ions, as well as Cu_2^+ and Cu^{2+} ions.

Synonym: cupric sulfide

Uses

Copper(II) sulfide is used in antifouling paints; in aniline black dye for dyeing of fabrics; and in the preparation of catalysts for organic reactions. It occurs in nature as the mineral covellite.

Physical Properties

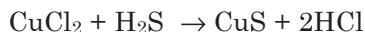
Black monoclinic or hexagonal crystals or powder; density 4.6 g/cm^3 ; refractive index 1.45; hardness 1.8 Mohs; decomposes at 220°C ; insoluble in water, ethanol and alkalis. $K_{\text{sp}} 8.0 \times 10^{-34}$; soluble in nitric acid, ammonium hydroxide and potassium cyanide solutions; also soluble in hot hydrochloric and sulfuric acids.

Thermochemical Properties

ΔH_f°	-12.7 kcal/mol
ΔG_f°	-12.8 kcal/mol
S°	15.9 cal/degree mol
C_p	11.43 cal/degree mol

Preparation

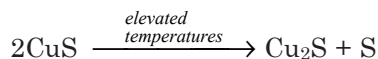
Copper(II) sulfide is produced from its natural mineral covellite. In the laboratory it is prepared by passing hydrogen sulfide into an aqueous solution of copper(II) salts:



Reactions

Copper(II) sulfide oxidizes to copper(II) sulfate in moist air. The compound, however, is stable in dry air at ordinary temperatures.

When heated strongly in the absence of air, it loses sulfur, forming copper(I) sulfide:



When heated with hydrogen below 600°C, it produces copper(I) sulfide. The presence of a small amount of sulfur enhances the yield of copper(I) sulfide.

Analysis

Elemental composition: Cu 66.46%, S 33.54%.

The compound may be identified by x-ray analysis. The copper content may be analyzed by AA, ICP, or x-ray fluorescence techniques.

CURIUM

[7440-51-9]

Symbol: Cm; atomic number 96; atomic weight 247; a radioactive transuranium actinide series element; electron configuration [Rn]5f⁷6d¹7s²; most stable valence state +3; most stable isotope Cm-247. Curium isotopes, half-lives and decay modes are:

Isotope	Half-Life	Decay Mode
Cm-238	2.5 hr	electron capture, alpha decay
Cm-239	3 hr	electron capture
Cm-240	26.8 days	alpha decay
Cm-241	35 days	alpha decay
Cm-242	163 days	alpha decay
Cm-243	32 yr	alpha decay
Cm-244	18.1 yr	alpha decay
Cm-245	9,320 yr	alpha decay
Cm-246	5,480 yr	alpha decay
Cm-247	1.67x10 ⁷ yr	alpha decay
Cm-248	4.7x10 ⁵ yr	alpha decay
Cm-249	65 min	beta decay

History, Occurrence, and Uses

Curium was discovered by Seaborg, James, and Ghiorso in 1944 during chemical fractionation of plutonium irradiated with alpha particles (32 MeV). The element was isolated in hydroxide form by Werner and Perlman in 1947 in microgram amounts, and later in 1950 by Crane, Wallmann, and Cunningham in elemental form. Crane *et al.* also studied its magnetic susceptibility and assigned 5f⁷ electron configuration to this element, analogous to 4f⁷ configuration of the element gadolinium in the lanthanide series. This man-made element was named curium in honor of Marie and Pierre Curie.

Curium does not occur in nature. Even if it had occurred in the primordial age of earth, its longest lasting isotope, Cm-247 (half-life of 17 million years),

would almost have fully disintegrated during the more than three billion years of earth's existence.

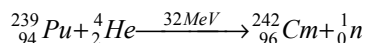
The element does not have any important commercial applications. Its isotopes Cm-242 and Cm-244 have potential applications to generate thermoelectric power for operation of instruments in space ships.

Physical Properties

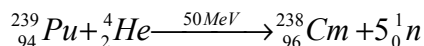
Silvery metal; density 13.51 g/cm³ (calculated); atomic volume 18 cm³/mole; melts in the range 1,300 to 1,380°C; magnetic susceptibility 12.2x10⁻⁸cgs units/mole at 25°C; dissolves in mineral acids.

Production

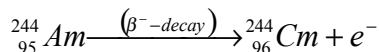
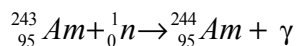
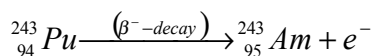
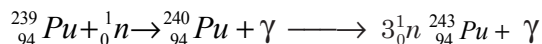
Curium can be synthesized in a nuclear reactor by several methods. The first synthesis involved alpha particle bombardment of plutonium-239:



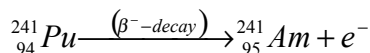
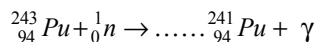
It may be synthesized by several other methods. Curium isotopes of lower mass numbers may be obtained by charged particle bombardments of plutonium-239:

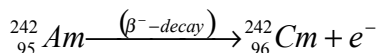
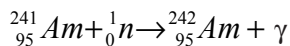


Curium-244 isotope may be obtained by irradiation of plutonium-239 by thermal neutrons:



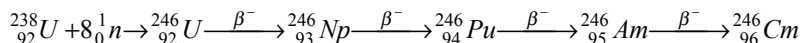
Curium-242 isotope may be obtained in the same way from plutonium-239 by successive neutron capture and β^- decay:





Also, higher isotopes of curium may be produced from curium-242 by neutron capture reactions.

The heavier isotopes of the element may result from rapid neutron capture process caused by intense neutron fluxes from thermonuclear explosions, followed by a series of β^- -decay (Cunningham, B.D. 1968. Curium. In *Encyclopedia of Chemical Elements*, ed. C. A. Hampel, pp. 173–177. New York: Reinhold Book Corp.)



Chemical Properties

Most properties are similar to the rare-earth analog gadolinium that has 7f electrons. The trivalent oxidation state (Cm^{3+}) is most stable. The metal is reactive, being more electropositive than aluminum.

Curium metal is stable at ambient temperature, but oxidizes on heating to curium(III) oxide, Cm_2O_3 .

When curium is heated with fluorine at 400°C, the product is CmF_4 , a tetravalent curium compound. However, heating with other halogens yields trivalent halides, CmX_3 . Similarly, when heated with hydrogen chloride gas at 500°C, the product is curium(III) chloride, CmCl_3 .

Curium metal liberates hydrogen from dilute acids, forming the trivalent, Cm^{3+} ion in the solution.

Many compounds of curium are known. They include the oxides, CmO_2 and Cm_2O_3 , fluorides CmF_4 and CmF_3 , other halides, CmX_3 ; hydroxide, $\text{Cm}(\text{OH})_3$, and oxalate $\text{Cm}_2(\text{C}_2\text{O}_4)_3$. The oxide, hydroxide, fluoride, and oxalate salts are insoluble in water and may be obtained by precipitation reactions.

Health Hazard

Curium may be absorbed into the body and can accumulate in the bone. Exposure to its radiation can destroy the red cell-forming mechanism.

CYANIC ACID

[75-13-8]

Formula: HCNO ; MW 43.03;

Structure: $\text{N}\equiv\text{C}-\text{O}-\text{H}$

Synonym: hydrogen cyanate

Uses

The compound has limited applications, primarily in the synthesis of cyanate salts.

Physical Properties

Colorless liquid or gas; pungent odor; density 1.14 g/mL at 20°C; solidifies at -86°C; boils at 23.5°C; dissolves in water (decomposes on standing); soluble in benzene, toluene and ether.

Thermochemical Properties

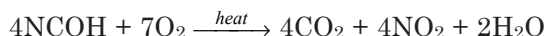
ΔH_f°	-36.90 kcal/mol
ΔG_f°	-28.0 kcal/mol
S°	34.6 cal/degree mol

Preparation

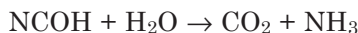
Cyanic acid is prepared in the laboratory by dry distillation of cyanuric acid, $C_3N_3(OH)_3$.

Reactions

Cyanic acid decomposes on heating. Rapid heating may cause explosion. When heated to high temperatures, it decomposes forming carbon dioxide, water, and nitrogen oxides:



It dissolves in water decomposing to carbon dioxide and ammonia. Although the reaction occurs at ordinary temperatures, it is slow in dilute aqueous solutions at ice temperature.



The compound polymerizes on standing, forming cyanuric acid, an oxygen heterocyclic compound, 1,3,5-trioxane-2,4,6-triimine, $C_3H_3N_3O_3$.

Analysis

Elemental composition: C 27.91%, H 2.34%, N 32.56%, O 37.19%.

Cyanic acid may be determined in benzene or toluene solution by GC either using an FID or, alternatively, an NPD measuring in nitrogen mode. Also, it may be identified by GC/MS; the molecular ion should have the mass 43.

CYANOGEN

[460-19-5]

Formula: C_2N_2 ; MW 52.035

Structure: $N \equiv C - C \equiv N$, linear; two isomers have been detected (isocyanogen is $C = N - N = C$); both are highly unstable.

Synonyms: ethanedinitrile; oxalic acid dinitrile; dicyan; oxalonitrile

Uses

Cyanogen has limited applications, the most important of which are in organic synthesis. Also, it is used in welding metals; as a fumigant; and in some rocket propellants.

Physical Properties

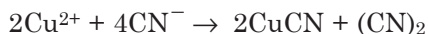
Colorless gas; almond-like pungent odor; burns with a pink flame with bluish tinge; density 2.283 g/L; liquefies at -21.1°C ; vapor pressure 635 torr at -25°C ; solidifies at -27.9°C ; critical pressure 59.02 atm; slightly soluble in water (about 400 mL gas at NTP dissolves in 100 mL water or 0.85 g/100 mL water) soluble in alcohol and ether.

Thermochemical Properties

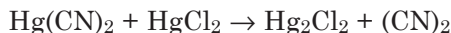
ΔH_f°	73.84 kcal/mol
ΔG_f°	71.07 kcal/mol
S°	57.8 cal/degree mol
C_p	13.6 cal/degree mol
ΔH_{fus}	2.06 kcal/mol

Preparation

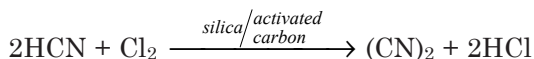
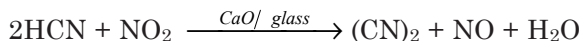
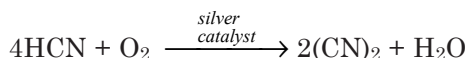
Cyanogen is prepared by the slow addition of potassium cyanide solution to a solution of copper(II) salt, such as copper(II) sulfate or chloride:



Cyanogen also may be prepared by the reaction of mercuric cyanide with mercuric chloride. Dry cyanogen gas may be obtained by this process:



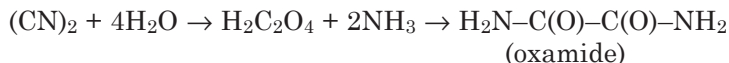
Cyanogen may be prepared by oxidation of hydrogen cyanide with oxygen, nitrogen dioxide, chlorine, or another suitable oxidizing agent, using various catalysts:



Reactions

Although cyanogen has a positive heat of formation (ΔH_f° 73.84 kcal/mol), the compound is unusually stable. In aqueous solution it is hydrolyzed slowly

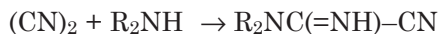
forming oxalic acid and ammonia, which combine to form oxamide:



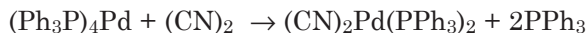
In basic solution, cyanogen dissociates rapidly, forming cyanide and oxy-cyanide salts:



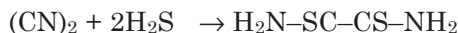
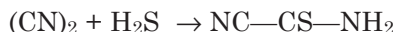
Reaction with ammonia yields 5-cyanotetrazole, a nitrogen heterocyclic ring compound. Reactions with alkyl amine, RNH_2 , yield dialkyloxalamidines $\text{RNHC}(=\text{NH})\text{CH}(=\text{NH})\text{NR}$; with dialkylamine, R_2NH , the product is N,N-dialkylcyanoformamidine:



Cyanogen can form mixed complexes with several transition metal complexes, partially displacing their ligands:



With hydrogen sulfide, the products are thiocyanofornamide, $\text{NCC}(=\text{S})\text{NH}_2$ and dithiooxamide, $\text{H}_2\text{NC}(=\text{S})\text{C}(=\text{S})\text{NH}_2$.



When heated at 500°C , it polymerizes into an insoluble product, paracyanogen $(\text{CN})_n$. On further heating to 850°C paracyanogen decomposes to cyanogen.

Reaction with fluorine yields the fluoroderivate, $\text{F}_3\text{CN}=\text{NCF}_3$.

Analysis

Elemental composition: C 46.16%, N 53.84%.

Cyanogen may be absorbed in ethanol or other suitable organic solvent and the solution analyzed by GC or GC/MS. The characteristic mass ions for identification by GC/MS are 52 and 26. Also, the compound may be analyzed by NMR.

Hazard

Cyanogen is a highly flammable gas. It forms explosive mixtures with air, LEL 6.6%, UEL 32% by volume. Reactions with oxygen, ozone, fluorine or other strong oxidizing agents can be explosive. Also, it can explode when exposed to spark, flame or heat.

Cyanogen is moderately toxic by inhalation. Exposure causes irritation of the eyes, nose and respiratory tract. A 10-minute exposure to about 10 ppm of the gas can manifest these irritant action in humans.

LC₅₀ (rat): 350 ppm in 1 hour.

CYANOGEN BROMIDE

[506-68-3]

Formula: CNBr; MW 105.92;

Structure: BrCN

Synonyms: bromine cyanide; bromocyan; bromocyanogen; cyanobromide

Uses

Cyanogen bromide is used in organic synthesis, as a rodent poison, and as a reagent for extracting gold as its cyanide salt.

Physical Properties

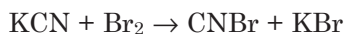
Colorless needles or cubic crystals; penetrating odor; density 2.015 g/cm³; melts at 52°C; boils at 61.4°C; soluble in water, alcohol and ether.

Thermochemical Properties

ΔH_f° (cry)	33.58 kcal/mol
ΔH_f° (g)	44.50 kcal/mol
ΔG_f° (g)	39.51 kcal/mol
S° (g)	59.35 cal/degree mol
C _p (g)	11.21 cal/degree mol

Preparation

Cyanogen bromide is obtained by the reaction of bromine with potassium cyanide or sodium cyanide:



Alternatively, it may be prepared by treating sodium bromide, sodium cyanide, and sodium chlorate with sulfuric acid.

Toxicity

The compound is highly toxic by all routes of exposure.

CYANOGEN CHLORIDE

[506-77-4]

Formula: CNCl; MW 61.47

Synonyms: chlorine cyanide; chlorcyan; chlorocyanogen; chlorocyanide

Uses

Cyanogen chloride is used in organic synthesis and as a tear gas in warfare.

Physical Properties

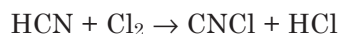
Colorless gas or liquid; density of the liquid 1.186 g/mL; solidifies at -6°C ; boils at 12.7°C ; soluble in water, alcohols, and ether.

Thermochemical Properties

ΔH_f° (l)	26.79 kcal/mol
ΔH_f° (g)	32.98 kcal/mol
ΔG_f° (g)	31.31 kcal/mol
S° (g)	56.45 cal/degree mol
C_p (g)	10.76 cal/degree mol

Preparation

Cyanogen chloride may be prepared by the action of chlorine with hydrogen cyanide:



It also may be prepared by the action of chlorine on a suspension of moist sodium cyanide in carbon tetrachloride at -3°C . The compound formed is purified by distillation.

Another method of preparation involves electrolysis of an aqueous solution of hydrogen cyanide and ammonium chloride.

Reactions

Cyanogen chloride reacts with caustic soda or caustic potash solution forming the alkali metal cyanide and the oxychloride:



It polymerizes on heating forming cyanuric chloride, $\text{C}_3\text{N}_3\text{Cl}_3$, a cyclic triazine compound.

The trimer of cyanogen chloride, $(\text{CNCl})_3$ reacts with fluorine in the presence of arsenic pentafluoride in chlorofluorocarbon solvent forming the complex $[\text{C}_3\text{N}_3\text{Cl}_3\text{F}][\text{AsF}_6]$.

Analysis

Elemental composition: C 19.54%, Cl 57.68%, N 22.79%. Cyanogen chloride may be analyzed by GC using an ECD or an FID. It may be identified by mass spectrometry. The characteristic mass ions are 60, 62, and 26.

Toxicity

Cyanogen chloride is highly toxic by all routes of exposure. It is a severe irritant to eyes, causing tears. Exposure to its vapors causes irritation of the respiratory tract and pulmonary congestion.

LC₅₀ (guinea pig): 5,500 mg/m³ in 2 minutes
 (1 ppm CNCl = 2.5 mg/m³ at NTP)

CYANOGEN IODIDE

[506-78-5]

Formula: CNI; MW 152.92

Structure: I-C≡N

Synonym: iodine cyanide

Physical Properties

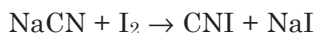
Colorless needles; pungent odor; acrid taste; density 1.84 g/cm³; melts at 146.7°C; vapor pressure 1 torr at 25°C; soluble in water, ethanol and ether.

Thermochemical Properties

ΔH _f [°] (cry)	39.72 kcal/mol
ΔH _f [°] (g)	53.90 kcal/mol
ΔG _f [°] (cry)	44.22 kcal/mol
ΔG _f [°] (g)	46.99 kcal/mol
S [°] (cry)	22.99 cal/degree mol
S [°] (g)	61.38 cal/degree mol
C _p (g)	11.54 cal/degree mol

Preparation

Cyanogen iodide is prepared by the reaction of iodine on sodium cyanide:



Toxicity

The compound is highly toxic by oral and subcutaneous routes. Ingestion can cause convulsion, paralysis, and respiratory failure.

LDL₀ oral (cat): 18 mg/kg

LD₅₀ subcutaneous (rat): 44 mg/kg

DEUTERIUM

[7782-39-0]

Symbol D or ^2_1H

An isotope of hydrogen; a stable, non-radioactive isotope; atomic number 1; atomic mass 2.014; molecular weight (for the diatomic heavy hydrogen molecule) 4.028.

Synonym: heavy hydrogen

History, Occurrence, and Uses

Rutherford predicted the existence of this heavy isotope of hydrogen in

1920. It was detected by Urey, Brickwedde and Murphy in 1932. It occurs in all natural compounds of hydrogen including water, as well as in free hydrogen molecules at the ratio of about one part per 6,000 parts hydrogen. The principal application of deuterium is in tracer studies for measuring rates and kinetics of chemical reactions. It also is used in thermonuclear reactions; and as a projectile in cyclotrons for bombardment of atomic nuclei to synthesize isotopes of several transuranium elements. Deuterium oxide, D_2O , or heavy water is used as a neutron moderator in nuclear reactors.

Physical Properties

Colorless, odorless gas; flammable; density of liquid deuterium at $-253^{\circ}C$ 0.169 g/mL; viscosity 12.6×10^{-5} poise at $27^{\circ}C$; liquefies at $-249.5^{\circ}C$; solidifies at $-254.4^{\circ}C$ at 121 torr; critical temperature $-234.75^{\circ}C$; critical pressure 16.43 atm; practically insoluble in water (3.4 mg D_2/L at $20^{\circ}C$).

Preparation

Deuterium may be prepared by several methods. Urey's first method of preparation involved fractional distillation of a very large amount of liquid hydrogen. It also may be produced by electrolysis of heavy water obtained by H_2S/H_2O exchange process. It may be obtained by continued, long-time electrolysis of ordinary water in which light water molecules are split first, thus concentrating deuterated oxygen in the residual liquid. Also, deuterium in high purity may be separated by thermally induced diffusion processes.

Reactions

The chemical reactions are very much similar to hydrogen (see Hydrogen). Deuterium undergoes exchange reactions instantly with hydrogen. Thus, mixtures of heavy water and water immediately form HDO. Similar exchange reactions occur in a number of hydrogen containing solutes dissolved in D_2O or mixtures of D_2O-H_2O . Such exchange reactions, however, are very slow in substances that contain carbon-hydrogen bonds.

Analysis

Deuterium may be analyzed from density measurements of waters. A confirmation method recommended here is GC mass spectrometry. Deuterium is burned in oxygen (or air) to form D_2O which may be separated with helium on a GC column (of intermediate polarity) and identified from its mass spectra. The mass to charge ratio of the molecular ion is 20. Additionally, deuterated products obtained by exchange reactions with hydrogen containing substances (other than those containing C—H bonds) may be separated on a capillary GC column and identified by mass spectrometry.

Hazard

Deuterium is a flammable gas. It forms explosive mixtures in air in between 5 to 75% by volume in air. The autoignition temperature is $585^{\circ}C$. Precautionary measures for handling this gas should be similar to those for hydrogen.